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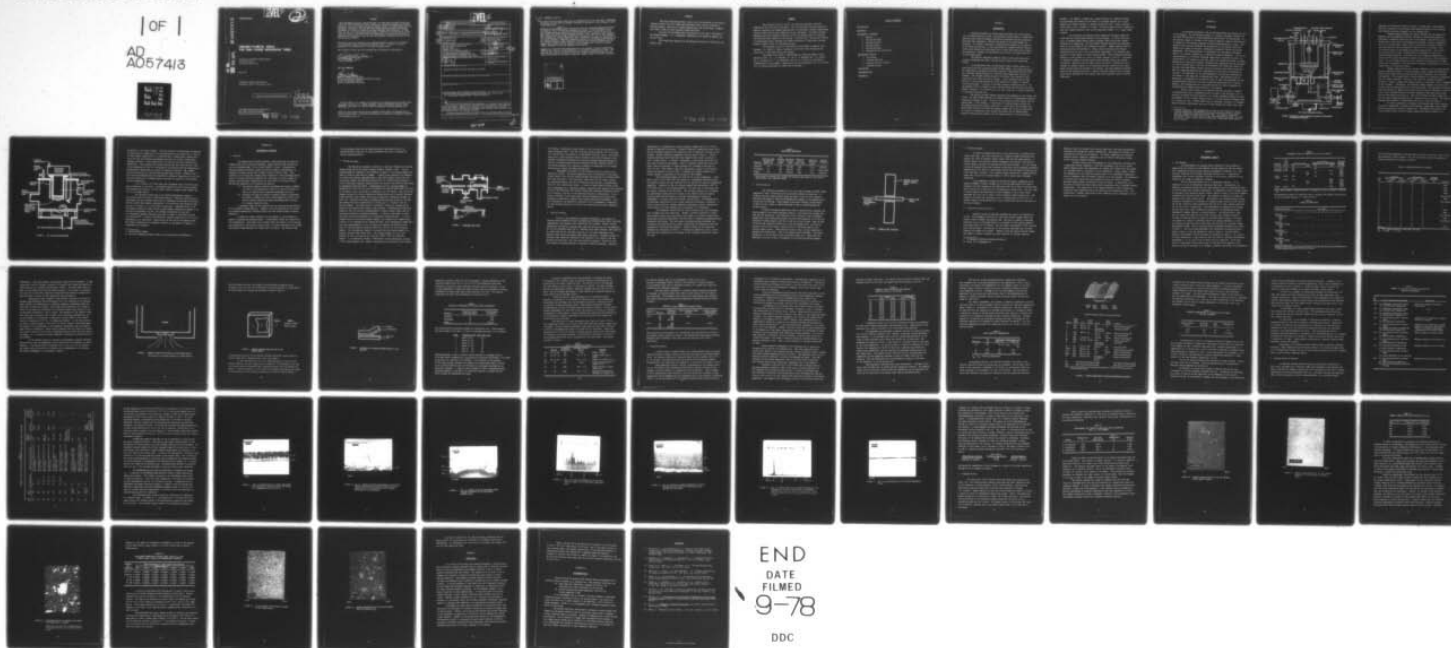
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**CERAMIC-TO-METAL SEALS
FOR HIGH POWER MICROWAVE TUBES**

*BATTELLE, COLUMBUS LABORATORIES
505 KING AVENUE
COLUMBUS, OHIO 43201*

MAY 1978

TECHNICAL REPORT AFML-TR-78-31
Final Report — May 15, 1976 - March 1, 1978

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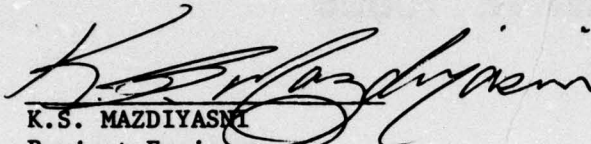
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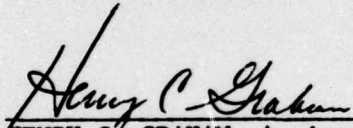
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This technical report has been reviewed and is approved for publication.


K.S. MAZDIYASN
Project Engineer

FOR THE COMMANDER


HENRY C. GRAHAM, Acting Chief
Processing and High Temperature Materials Branch
Metals and Ceramics Division
Air Force Materials Laboratory

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The objective of the program was the development of a material process capability for metal-to-ceramic sealing used in high-power cross-field amplifier (CFA) microwave tubes. The specific objective was to develop the ion plating process to deposit multilayered metallic coatings onto the highest purity available beryllium oxide (BeO) and aluminum nitride (AlN) substrate materials. A satisfactory copper/molybdenum-to-beryllia bond was achieved without the use of an active metal adhesion aid such as titanium. An ion plating technique was developed (Continued)			

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20. ABSTRACT (cont'd)

for depositing two-layer films such as molybdenum and copper onto BeO. Subsequent evaluation of this metal-to-ceramic combination indicated a bond strength of over 140.32 Mega Pascal.

Diffusion bonds between copper tensile bars and the copper/molybdenum-coated BeO were made at 1223 K in both wet hydrogen and vacuum. A bond strength of over 140.32 Mega Pascal was obtained by vacuum bonding, while a value of only 52.6 Mega Pascal was obtained with hydrogen bonding. Weak interfacial bond strengths were obtained with ion plated three-layer coatings (Ti, Mo, Cu) on BeO, because of an ineffective cathode design and lack of available equipment to compensate for the design problems. Chemical composition analysis of an as-deposited coating by the energy-dispersive X-ray technique indicated that titanium diffused into the copper layer, which probably resulted in the formation of a brittle titanium-copper intermetallic and the observed weak adhesion.

Commercially available AlN powder which was hot pressed to form an engineering material was found to be unsatisfactory as a substrate alternative to BeO. The expected high thermal conductivity was not obtained, presumably because of the high oxide content of the powder (5 percent oxygen versus 0.3 percent expected).

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FOREWORD

This Final Engineering Report covers the work performed on the project "Ceramic-to-Metal Seals for High Power Microwave Tubes" and was prepared by Battelle Memorial Institute's Columbus Laboratories, 505 King Avenue, Columbus, Ohio 43201, under Air Force Contract F33615-76-R-5239.

The work was performed under the direction of Mr. Roy F. Wielonski as the Program Manager. K. S. Mazdiyasni, AFML/LLM was the Technical Manager for the Air Force.

This report was supported by the Laboratory Director's Fund and by the Project Fund.

PREFACE

This program proved to involve two tenacious problems, each more complicated than initially anticipated. The first problem developed around the apparent complexity and seeming impossibility of obtaining a suitable engineering structure when starting with commercial purity AlN powder. The second problem developed around the apparent inability of the ion plating process to produce the excellent bonds typical of the process. In particular, this was with respect to bonds between metal coatings and ceramic substrates or other metal coatings formed by means of the rf ion plating process.

The Statement of Work of the contract was modified to address these problems. Dr. Robert A. Rapp, a professor at The Ohio State University was utilized as a consultant during the program.

The author also wishes to acknowledge the following members of the Battelle staff: Dr. J. M. Blocher, Jr., Mr. M. F. Browning, Mr. J. S. Fippin, Mr. G. E. Hoover, Mr. P. E. Scheiderer, and Dr. R. R. Wills who contributed significantly to the program. Appreciation is also expressed to Dr. S. H. Gelles of S. H. Gelles Associates for analytical assistance.

TABLE OF CONTENTS

INTRODUCTION	1
BACKGROUND	3
EXPERIMENTAL PROCEDURE	8
1. Approach	8
2. Coating Equipment	9
3. Coating Procedure	11
4. Bond Evaluation	13
5. Bonding Equipment	15
6. Aluminum Nitride Fabrication	15
EXPERIMENTAL RESULTS	17
1. Ion Plating	17
2. Titanium Diffusion	26
3. Coating Structure Analysis	32
4. Aluminum Nitride	43
CONCLUSIONS	52
RECOMMENDATIONS	53
REFERENCES	54

SECTION I

INTRODUCTION

Metallized ceramics of various types are being used in the fabrication of microwave electron tubes. One particular design called a crossed-field amplifier tube relies on numerous electrically insulating and heat conducting beryllium oxide components. Beryllia was chosen for its high thermal conductivity. It, however, represents a potential health hazard in the event of an explosive tube failure. A less toxic material, aluminum nitride, theoretically could replace beryllium oxide since it would have similar heat conducting properties. However, the feasibility of its use in this application has not been demonstrated.

The beryllia components presently used are first metallized with a titanium, molybdenum and copper coating system by means of the sputtering process.

In the amplifier tube, the metallized ceramic surface supports an electrical delay line carrying microwave (8 GHz) energy. The coated insulators are simultaneously attached to the delay line and a copper water-cooling block by a diffusion bonding technique at relatively high temperature (1223 K) in hydrogen. The microwave energy carried by this delay line produces an electrical field just above the line's surface. A well collimated electron beam parallel to and passing through this field interacts to produce an increase in microwave energy. A portion of the beam constantly bombards the line. The heat generated must be removed by water cooling through the metallized beryllia-ceramic insulators. The reliability of the tube, therefore, is greatly dependent on the metal-to-ceramic bond.

The metal-to-ceramic bonding techniques vary, depending on the ceramic substrate. For high alumina materials, a process called the "moly-manganese approach" developed in Germany, is used. It relies on the reaction of metal oxides with the glassy phase in the alumina. A viscous melt is formed between the metal and the glassy phase of the ceramic around 1673 K in wet H_2/N_2 . Upon cooling, this glassy phase contracts less than the alumina ceramic and is then in compression. As a result a strong bond occurs between the ceramic and the applied metal. Another technique which competes with the former process is the "active metal

process". For example, titanium has a great affinity for ceramics and when placed between the ceramic and the metal to be bonded requires only a high temperature thermal treatment to produce the desired bond. Either technique can be used to join a ceramic to a metal. The active metal process is generally used with ceramic materials that do not form glassy phases, i.e., single phase ceramics.

Ion plating is the physical vapor deposition technique chosen for study with the "active metal process" in this program. It offers the potential of forming higher quality metal-to-ceramic bonds than either thermal evaporation or sputtering. The bond formed between substrate and condensate improves as the energy of the condensate increases. Higher energies improve coating-substrate interdiffusion. Energy levels associated with thermal evaporation are low (0.1-1 ev), and material deposited at low substrate temperatures in this manner is usually weakly bonded. Sputter-deposited material, however, is well bonded as a result of higher energies (1-100 ev). Increases in deposition energy to further improve bond strength require ion plating procedures. High-rate electron beam sources can supply a sufficient flux to surpass the sputter removal of the deposited material associated with these higher energy levels and produce a net coating. The high energies associated with the ion plating process are a result of applied substrate bias voltages which can be thousands of volts higher than those ordinarily used in sputter deposition.

SECTION II

BACKGROUND

As indicated previously, the ion plating process was selected for use in the program. The ion plating process is a recently developed variation of the basic PVD processes, vacuum evaporation (metallizing) and sputtering. In ion plating, Figure 1, the part to be coated is made the negative electrode and is placed in a low-pressure (vacuum) dc glow discharge, usually of argon. The positive ions from the discharge are accelerated by the electric field and bombard the surface of the part, continuously cleaning it before and during deposition. The coating material is evaporated into the gaseous discharge where it is ionized, primarily by a Penning ionization* mechanism. Ions of the coating material, in the glow discharge region which surrounds the part, are accelerated to all surfaces of the part across the cathode dark space (Crookes). Because most of the field gradient (voltage drop) associated with the discharge is across the dark space, the ions are accelerated and strike the surface of the part with high kinetic energy, typically forming a very adherent coating. Thus two competing phenomena are simultaneously occurring at the surface of the part: the deposition of the coating-material ions and the sputtering of the deposit by the argon and coating-material ions. The effective rate of deposition is determined by the relative rates of these two phenomena, and the coating-material deposition rate must exceed the sputtering rate to obtain a deposit. The cleaning action of the sputtering by the ions is important in establishing the adhesion and structure of the deposit.

When an oxide ceramic is the desired substrate on which to deposit an adherent metal film, consideration must be given to the following; (a) reaction of the metal with the substrate, (b) thermal expansion mismatch of metal and ceramic, and (c) surface charge build-up. To obtain metal-to-ceramic seals, it is typical to use a "primer layer" such as titanium, zirconium, or chromium. These so-called primer metals have such a high affinity for oxygen that, when

* Penning ionization: The ionization of an atom by the transfer of the excitation energy from a metastable atom whose excitation energy is greater than the ionization energy of the first atom. For example, argon has metastable states of 11.55 and 11.75 eV; the ionization energy of copper is 7.68 eV. Thus a copper atom colliding with a metastable argon atom is easily ionized.

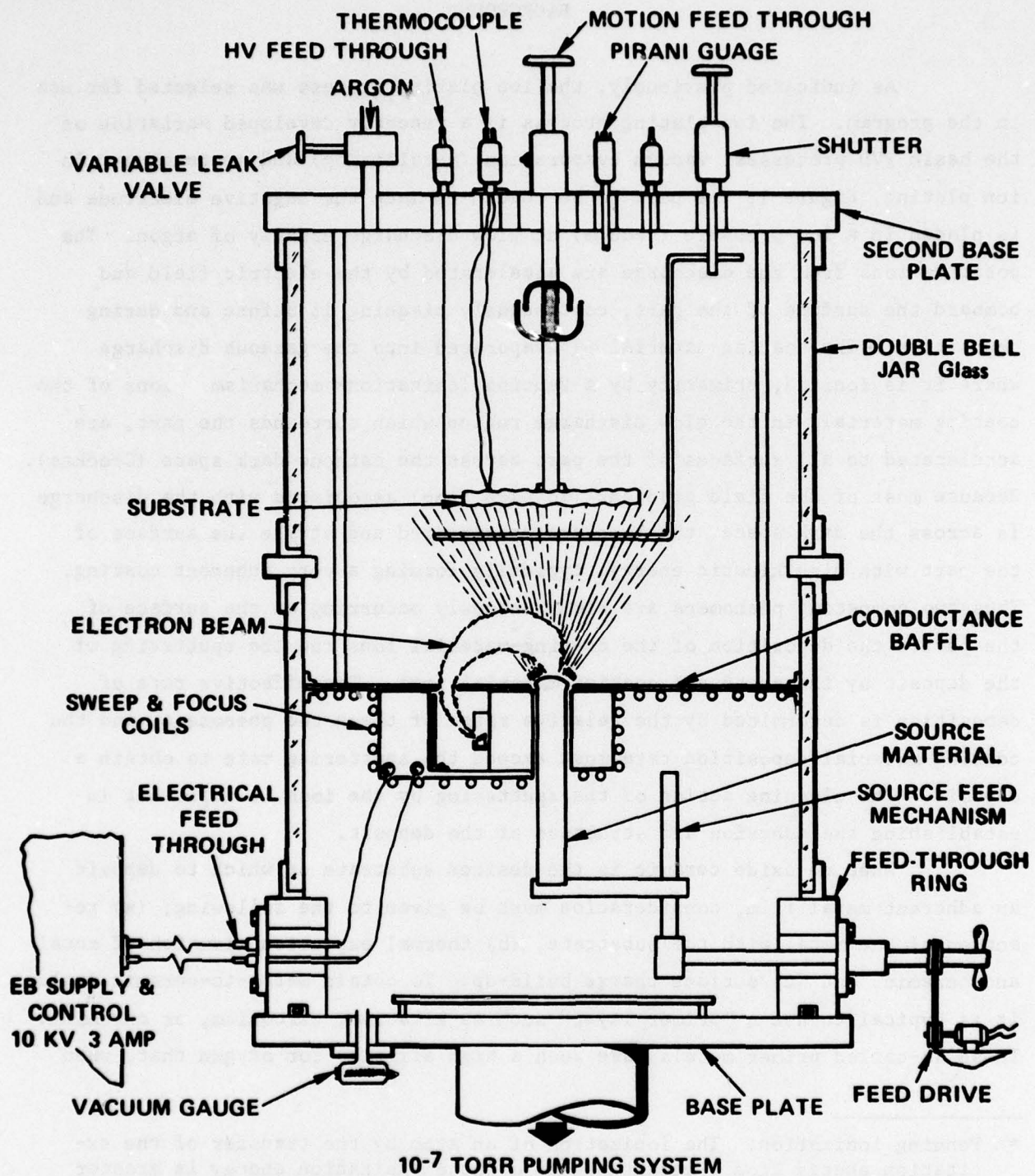


FIGURE 1. EXPERIMENTAL APPARATUS FOR ION PLATING BY HOT-FILAMENT ELECTRON BEAM TECHNIQUE

deposited, an interfacial transition region of ceramic-metal oxide develops. Once this transition is established, other nonactive metals can be deposited which develop high bond strengths with the "primer layer".

Thermal mismatch between the ceramic substrate and the depositing material can be accommodated through a selection of metals with thermal coefficients of expansion (TCE) near that of the ceramic. The TCE of titanium matches that of BeO better than chromium or zirconium. However, titanium, as part of a titanium/copper system, poses a problem with long-term reliability when deposited onto BeO and thermally cycled to 1173 K in hydrogen, since the diffusion which occurs weakens the ceramic/titanium bond. This problem can be alleviated by using a barrier layer of molybdenum to control the titanium/copper diffusion. It has been shown that substrate temperatures as high as 973 K² produce undesirable columnar grain structures in the molybdenum layer. The ion plating technique has the potential of minimizing the columnar structures of molybdenum, since the effective substrate temperatures, as well as energy levels, are typically higher.

Surface charge build-up on a ceramic substrate can be a severe problem during a deposition process. If not corrected, a space charge will develop in front of the ceramic and newly arriving ions will be repulsed, never reaching the substrate. To circumvent this, a radio frequency (rf) potential is impressed onto the ceramic substrate. Because of the nature of a plasma (a plasma is basically a diode), a negative dc plasma potential is developed. This is superposed on the rf signal. Consequently, the substrate remains negative for most of the rf wave cycle and goes positive for a very short time. Ions can arrive during the time the substrate is negative and electrons arrive when the substrate is positive. This is very satisfactory since electrons, because of their much smaller mass, are much more mobile than the ions. This then nullifies the space charge once each rf cycle, thereby allowing the ion plating process to proceed. The substrate holding device capable of withstanding the rf bias is shown in Figure 2.

It would be desirable to eliminate the titanium layer while retaining the barrier (molybdenum), provided that acceptable ceramic/metal bond strength could be maintained at elevated temperatures. Molybdenum would prevent a reaction between copper and BeO at higher temperatures which is known to be

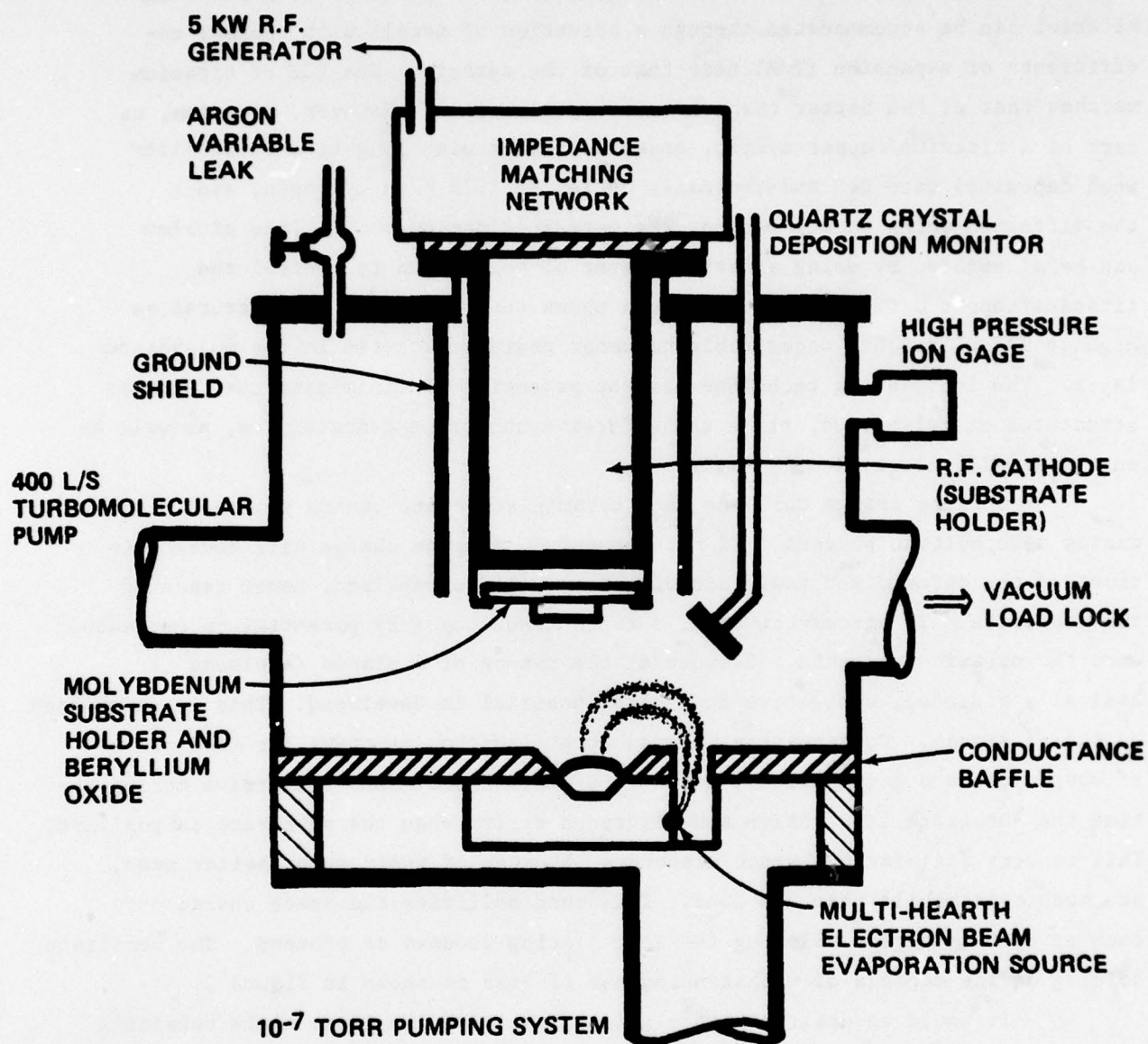


FIGURE 2. R.F. ION PLATING SYSTEM

detrimental to the bond strength. The bond strength of Mo/BeO might be improved by increasing the temperature of the BeO substrate during deposition to >1463 K. At these higher temperatures it is expected that a morphological change would occur and that the deposited molybdenum would have an equiaxed rather than columnar structure. These expectations are based on the work of Movchan and Demchishin¹. They specifically studied titanium and have shown that at a substrate temperature of 923 K or 48 percent of the absolute melting temperature), a morphological change begins to occur for deposited titanium. The columnar structure gives way to recrystallized equiaxed grain growth. Sherman et al.² have studied molybdenum and have identified a substrate temperature of 1473 K at which the transition to equiaxed growth initiates (51 percent of the absolute melting temperature).

D. E. Clark et al.³ have shown that molybdenum reacts with BeO along grain boundaries in the oxide. A molybdenum powder was used in their studies and sintered with the BeO. For Mo on BeO, tensile strength values ranged from 32.6 to 65.3 Mega Pascal.

The beryllium oxide used in the present experimental program is 99.5 percent pure and close to theoretical density. Beryllium oxide has major advantages over most ceramics when used as a substrate for microwave electronic devices, namely high thermal conductivity (2.4 watts/cm-K) and relatively high dielectric constant (6.1) at microwave frequencies*. Aluminum nitride is of low toxicity relative to BeO, and has a high thermal conductivity, making it an attractive replacement for BeO. The thermal conductivity of pure AlN (3.2 watt/cm-K) compares favorably with that of copper (4 watt/cm-K) and BeO (3.8 watt/cm-K)**. Values of the dielectric constant range from 8.5 to 9.14 at frequencies up to 1000 Hertz. These values are for AlN of the highest purity. The thermal conductivity is extremely sensitive to the amount of oxygen incorporated as an impurity.

* Brush Wellman Company

** Air Force Cambridge Research Report on AlN Properties and Reference 4.

SECTION III

EXPERIMENTAL PROCEDURE

1. Approach

The approach was directed primarily toward improving the metal-to-ceramic bond of the titanium, molybdenum, copper system on BeO, through the use of an electron-beam, rf ion plating (EBRFIP) Process. Molybdenum as presently deposited provides limited protection against interdiffusion of titanium and copper through the columnar structure barrier layer. This diffusion occurs along the columnar grain boundaries in the molybdenum barrier layer at the high processing temperatures, resulting in brittle, weakly adhering, titanium/copper intermetallics on both sides of the barrier layer. The specific approach to this problem was twofold:

- (1) Successively deposit titanium, molybdenum and copper by EBRFIP onto BeO at high temperature (≈ 1173 K) to obtain increased adhesion of titanium and an improved molybdenum structure.
- (2) Eliminate titanium and deposit successive layers of molybdenum and copper by EBRFIP onto BeO at high temperature (≈ 1173 K) to obtain a highly adhering and dense molybdenum layer followed by a copper conductive layer.

A secondary aspect of the approach was the selection and fabrication of an alternate ceramic material. Samples of AlN were prepared by the vacuum hot pressing commercially available powder with and without oxygen scrubbing additives.

To meet the overall objective of the program, it was necessary to modify an existing ion plating system. A considerable effort was required for this modification. This effort was justified since the quality of the coatings and reliability of the process require control of vacuum environment and certain specialized system additions not commercially available. The electron beam

rf ion plating system that was developed meets these needs and will be described below, along with a typical procedure used for ion plating the various coating materials.

2. Coating Equipment

The deposition equipment consists of a specially designed ion plating vacuum system and air-to-vacuum transfer chamber, Figures 2 and 3. The ion plating system is composed of two chambers, an upper or ion plating chamber and lower or electron beam emitter chamber. A baffle plate separates the chambers, yet allows the electron beam generated in the lower chamber to pass into the ion plating chamber and evaporate material held in a water-cooled crucible. A 2,000 liter/second diffusion pumping system can maintain the electron beam source at appropriate pressure levels. Simultaneously the ion plating chamber is evacuated by a 400 liter per second turbomolecular pump allowing argon flow rates of 168 Pascal liters per second at pressures up to 3.99 Pascal. The ion plating chamber contains the sputter cathode and ground shield with a special substrate holder mounted in the cathode that accepts substrates transferred through the load lock. Suitable shuttering, for predeposition-sputter-cleaning of the BeO, and evaporation-source conditioning of the material is located in the ion-plating chamber. The baffle plate is machined to provide an opening for exposure of the electron beam source to the crucible. Monitoring and control of evaporant from the source is accomplished by a quartz crystal sensor and its associated electronic processing equipment. A shutter is provided to shield the sensor during conditioning of the evaporation source material. A 50.8 cm diameter door on the coating chamber supports the vacuum-to-air chamber which consists of an intermediate and loading sections. This intermediate chamber has a 15.24 cm inside diameter, is 25.4 cm long, and contains two stainless steel rails for transporting the substrate plate into and out of the ion plating chamber. The intermediate chamber is isolated from the loading chamber by a manually operated high vacuum valve. The loading chamber is 15.24 cm in diameter by 30.48 cm long and also contains similar rails for substrate support. A rod operating through a linear-motion vacuum feedthrough, mounted on the loading chamber door, permits transporting the substrate to the cathode

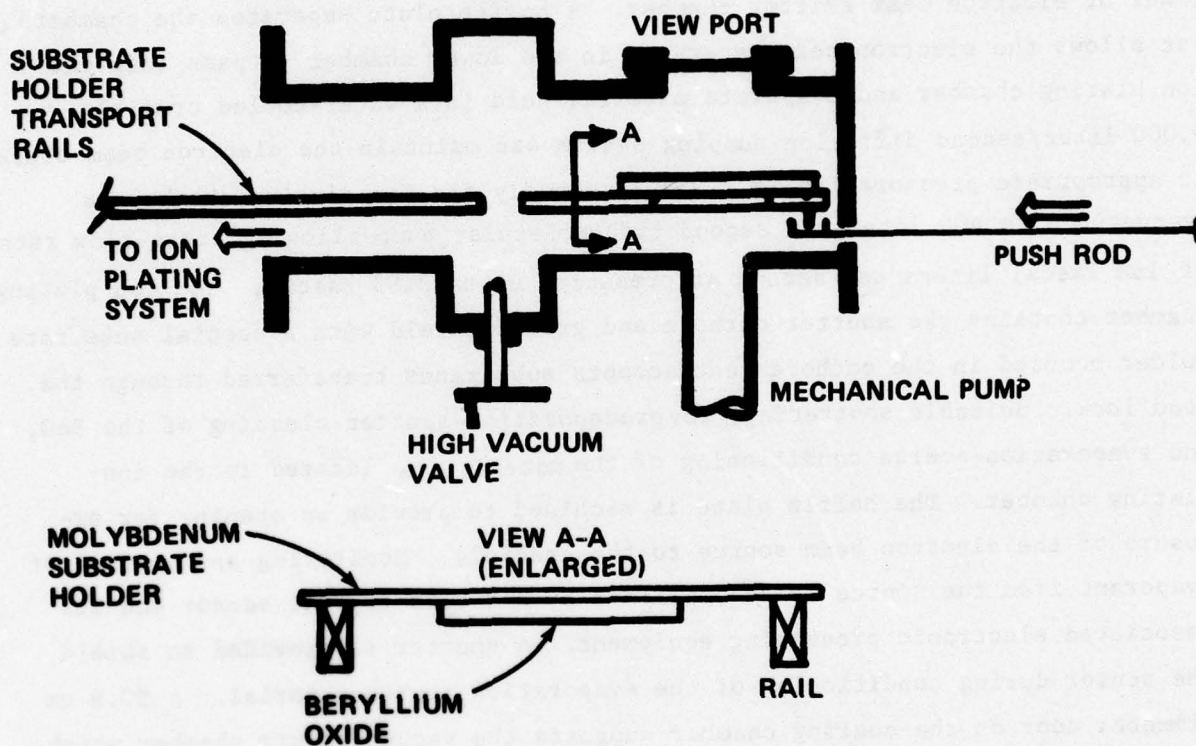


FIGURE 3. VACUUM LOAD LOCK

for coating. Appropriate vacuum levels in the load lock are obtained by a small mechanical pump. The radio frequency power necessary for ion plating onto the beryllia is provided by an adjustable 5000 watt source. This power supply has a fixed internal output resistance which must be matched to the variable resistance associated with the gas discharge generated during ion plating. A manually-controlled power matching network connected directly to the cathode performs this function in addition to measuring the dc voltage developed as a result of plasma rectification.

Measurement and control of the depositing film is critical for a repeatable process. The actual deposition cycle is monitored by the quartz crystal sensor, with the data being obtained and processed in an Inficon XMS-3 thin film controller. This controller, when used with the sensor crystal, can accurately measure the rate of evaporation and maintain a predetermined value for the electron beam source. A total of three material system cycles can be programmed (as to material density, deposition rate desired, film thickness, etc.) into the controller for control during their respective deposition cycle. In ion plating, a portion of the deposited material is resputtered. A calibration procedure is then used which involves determining the actual film thickness as deposited on glass slides through mechanical measurement. With this information, the deposition controller can be programmed to compensate for the sputtered portion of the final film thickness and provide repeatable results.

3. Coating Procedure

As part of the deposition procedure development, the effects of varying certain parameter values (including ion plating coating rates, substrate temperatures, and substrate bias conditions) were studied. Several initial experiments involved ion plating rates from 480 700 A/min for Ti, 423-3060A/min for Mo, and 2500-3500 A/min for Cu. Specific rates were selected, 1450 A/min for Ti, 2400 A/min for Mo, and 3000 A/min for Cu, for later experiments since adherent films could be produced under these conditions. Analogous studies of substrate bias conditions resulted in the selection of an initial -250 volt sputter etch bias and a -250 volt bias during ion plating. The use of this bias during ion plating resulted in beneficial substrate heating. Substrate

temperatures, as determined by optical pyrometry ranged from 1173 to 1273 K sputter etching and ion plating. Presently substrate temperatures above 1273 K are not attainable because of the materials used to fabricate a portion of the cathode. Typical deposition parameters used are given in Table 1. The as-received beryllium oxide substrates were lapped on both sides to produce a 1270 Å surface finish. A solvent, a detergent, a water rinse and an air dry were used to clean all BeO wafers. Prior to coating, wafers were placed in a quartz tube and inserted in a muffle furnace for a minimum of one hour at 1273 K in air. Upon removal, they were individually loaded on the substrate holder and inserted in the air lock. A maximum of 5 minutes elapsed from furnace removal to pump down of the vacuum air lock chamber.

The following procedure was used for all of the experiments. A BeO wafer ($2.54 \times 2.54 \times 0.051 \text{ cm}^3$) was mounted on a molybdenum substrate holder. The substrate holder was then inserted into the cathode for sputter cleaning and deposition. Pressures in the ion plating chamber were maintained at 10^{-4} to 10^{-5} Pascal prior to any coating operation. The next step in the process was the sputter cleaning of the BeO wafer. Once an argon pressure of 3.99 Pascal was established, application of rf power to the cathode initiated sputter cleaning conditions and heating of the BeO simultaneously through ion bombardment. At power levels of 750 watts (93 watts/cm^2), the temperature of the BeO wafer stabilized at 1173 K after typically 20 minutes of operation. A shutter placed below the cathode permitted simultaneous sputter cleaning and conditioning of the BeO substrate and the material to be evaporated.

All parameters controlling the electron beam source were programmed into the XMS-3 thin film controller. However, provision existed for reverting to manual control when new material was added to the electron beam source, permitting controlled premelting of the new stock to eliminate outgassing during subsequent ion plating. Once the sputter cleaning had been performed, the controller then established the proper conditioning and evaporation rates and sequentially controlled each material. Typical values for the deposition parameters are presented in Table 1. Following the deposition cycle, a cool-down time was initiated prior to removal of the substrate through the vacuum-air lock.

TABLE 1.
DEPOSITION PARAMETERS

Material	Electron Beam Evaporation Power*, kw	Ion Plating RF Bias, watts	Developed DC Bias, volts	Effective Coating Rate, A/min	Argon Gas Pressure, Pascal	Coating Thickness, A
Titanium	3-4	750	300-500	1500	3.99	250-350
Molybdenum	6-7	750	300-500	2500	2.66	7000-10,000
Copper	4-5	750	300-500	3000	2.66	~100,000

* The control of coating rate caused the electron beam power to fall into a range rather than specific values.

4. Bond Evaluation

The evaluation procedure for all ion plated coatings included visual examination under a microscope and a qualitative adhesion scrape test. A surgical stainless steel scalpel blade was used to test the film integrity. The blade was angled at about 20-30 degrees with respect to the substrate and forced into the coating. Since copper is the final coating, strong rating is given if only copper is removed and weak if BeO is exposed during the scrape testing.

A tensile testing procedure was used to quantitatively determine the bond strength of ion plated coatings, Figure 4. Two tensile bar designs were used for the evaluation. The first was a 5.08 cm long by 0.953 cm diameter oxygen free, high conductivity copper rod with a grid machined in one end consisting of sixteen squares 0.102 cm x 0.102 cm x 0.102 cm high. Near the end of the rod and centrally located is a 0.318 cm diameter hole. The hole at the end of the rod was used to secure a pin to a universal mount in the Instron tensile tester. These rods were used to test all high temperature hydrogen and vacuum bonds. This is the design used by Warnecke. The second design was a 3.81 cm long x 0.318 cm diameter copper rod. These rods were machined on one end to help in alignment of the coated BeO during bonding.

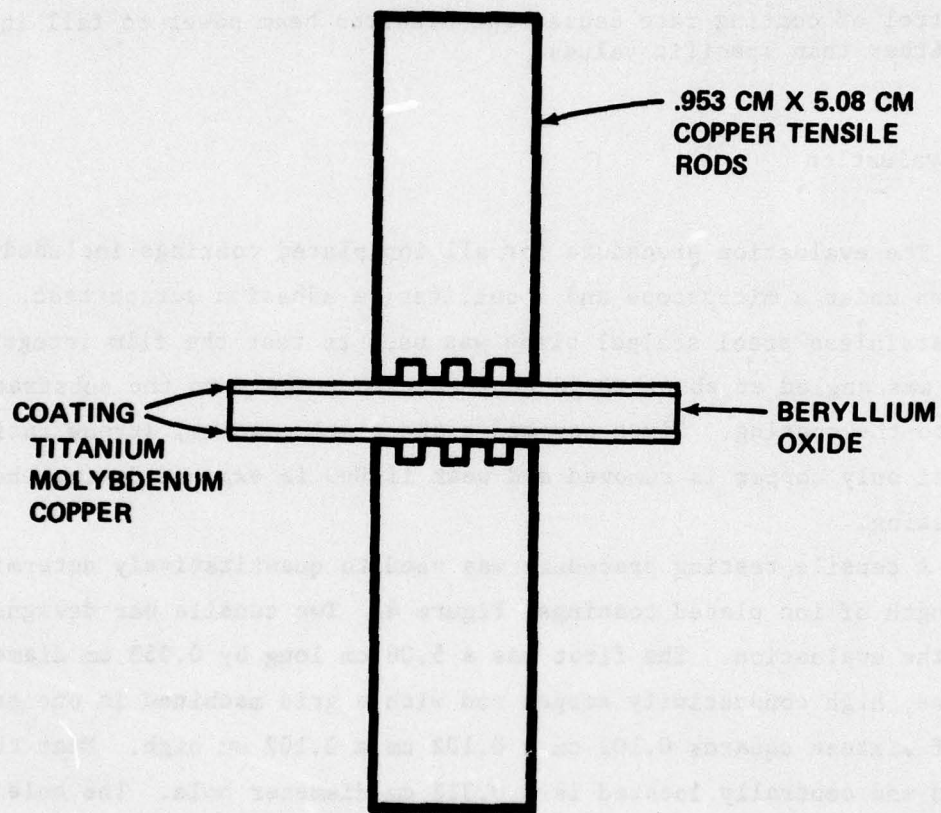


FIGURE 4. TENSILE TEST FIXTURE

5. Bonding Equipment

In order to perform bond tests on the coated BeO, two bonding techniques were used. The first consisted of a copper-to-copper diffusion bond between the 0.953 cm diameter copper tensile rods and the copper deposit. A special fixture was used that allowed alignment of the tensile rods and provided a means to preload the tensile rods and coated ceramic. A 71.12 cm long by 5.08 cm diameter Vycor tube provided an enclosure for the hydrogen atmosphere. Temperatures up to 1223 K at the bonding fixture were obtained by inserting the Vycor tube into a furnace. Also, several copper-tensile-rod to deposited-film bonds were effected in a vacuum furnace at 1223 K rather than a hydrogen atmosphere.

A low temperature (below 533 K) bond utilizing a commercial epoxy adhesive 3MEC286* (tensile strength of 157.9-166.6 Mega Pascal) was used to establish the bond strength of the deposited films (Ti on BeO, Ti and Mo on BeO and Ti, Mo and Cu on BeO) prior to the hydrogen or vacuum cycle. For this test, a V-block fixture was fabricated to allow alignment of up to five coated specimens with the 3.81 cm long x 0.318 cm diameter copper tensile rods. The curing of the epoxy was performed in air at temperatures of 450-477 K. An Instron tensile testing machine with chart recorder was used for evaluation of the bond strengths.

6. Aluminum Nitride Fabrication

Standard vacuum hot-pressing equipment was used in the fabrication of AlN. This equipment consisted of a mild steel vacuum chamber which contained a heater assembly and pressure ram. The unit is capable of applying pressures of up to 175.4 Mega Pascal on a specimen at 2227 K while maintaining vacuum levels of 10^{-4} Pascal. For this study, AlN powder** of 99.7 percent purity was procured. The analysis of the supplier indicated that the major impurity was oxygen (0.3 percent). However, inert gas fusion analysis showed the powder to contain 5 percent O₂ rather than the 0.3 percent expected.

* 3M (Minnesota Mining and Manufacturing Co.)

** Cerac, Inc., Milwaukee, WI.

Samples of AlN, hot pressed under various conditions, were metallographically sectioned and polished for optical examination. Measurements of thermal conductivities were made by two methods: (1) thermal comparison with standard material using a commercial comparator, and (2) thermal diffusivity using a pulsed laser and infrared detector.

Thermal conductivity measurements at room temperature were made with a commercial thermal comparator. With this instrument, the tip of a probe heated slightly above room temperature is brought into contact with the surface of a specimen which is originally at room temperature. After contact is made, the temperature of the probe tip quickly drops to an intermediate temperature which is dependent upon the thermal conductivity of the specimen. The comparator is calibrated by noting the probe temperature drops for several standard materials whose thermal conductivity values are known. A calibration curve may then be constructed which relates probe temperature drop to specimen thermal conductivity. The conductivity of an unknown specimen is then determined by noting the probe temperature drop and consulting the calibration curve. The uncertainty in thermal conductivity values obtained by this technique is in the range of 10 to 20 percent.

SECTION IV

EXPERIMENTAL RESULTS

1. Ion Plating

The experimental ion plating results obtained in the program indicated that the adhesion of the Cu/Mo/Ti coating system onto BeO was weak at best; depending on the particular deposition parameters selected, i.e., coating rate, substrate bias voltage, argon gas pressure, etc. A qualitative scrape/peel test usually indicated a failure at one or more interfaces of the system for the range of parameters evaluated.

The ion plating coating rate is a complicated quantity. It is affected by all of the parameters previously mentioned. Consequently, the effective ion plating coating rate for each material used as a metallizing layer on the BeO wafers was initially determined. As different rf bias (voltage) powers are applied to the substrate holder, sputter removal of part of the total normally condensed film thickness takes place. This removal is sensitive to argon gas pressure and rf bias voltage levels. The effective ion plated coating rate was, therefore, determined as a function of a specific argon pressure (0.666 Pascal), two values of electron beam evaporation rate and two rf bias voltage conditions for Ti, Mo, and Cu, respectively. Once determined, the effective ion plating coating rates were used to establish conditions for an experimental matrix developed to examine effects on coating adhesion. Two coating rates, high and low, along with high and low rf bias voltage levels formed the matrix. In order to keep the matrix as simple as possible while allowing it to serve its purpose as a means of isolating desired ion plating conditions, a fixed ion plating coating rate and rf bias power were selected for the final copper metallization layer. The ion plating coating parameters determined are listed in Table 2. The ion plating experiments were performed utilizing the matrix given in Table 3, with the parameters listed in Table 2. The qualitative adhesion (scrape/peel) results obtained are displayed in Table 4. As a result of these experiments, a high substrate bias was found to increase film adhesion. Experiments 1, 2, 10, and 16 are the basis for this deduction. In the next series of experiments, bias power levels of 1000 watts were applied to the beryllia during ion plating, in an attempt to improve the results of the adhesion.

TABLE 2
PARAMETER VALUES FOR MATRIX USED TO STUDY ADHESION

Coating Material	Gas Pressure, Pascal	RF Bias Power,		Ion Plating Coating Rate, Angstrom/Min		RF Bias*
		Low	High	Low	High	Voltage Low/High
Titanium	0.666	300		480		-1400
Titanium	0.666	300			948	-1400
			600	348		-1800
			600		700	-1800
Molybdenum	0.666	300		423		-1400
	0.666	300			2060	-1400
			600		309	-1400
			600		1477	-1800
						-1800
Copper	0.666	300			2500	-1400

* RF Bias Voltage = plasma rectified or induced D.C. bias, as result of applied RF

The experimental matrix of conditions used to optimize the adhesion and structure of the ion plated coatings, is shown in Table 3.

TABLE 3
MATRIX OF CONDITIONS

Material/Parameter	Run Number															
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Titanium																
Coating rate																
High	+	+	+	+	+	+	+	+								
Low									-	-	-	-	-	-	-	-
Titanium																
RF bias voltage																
High	+				+		+	+		+	+		+			+
Low		-	-	-		-			-			-		-	-	
Molybdenum																
Coating rate																
High	+	+			+	+					+			+	+	+
Low			-	-			-	-	-	-		-	-			
Molybdenum																
RF bias voltage																
High	+	+	+					+		+		+		+		+
Low				-	-	-			-		-		-		-	
Copper coating rate	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*

* 2500 Angstrom/minute at 300 watts RF bias.

The ion plating experiments were performed utilizing this matrix, Table 3 with the parameters listed in Table 2 and the qualitative adhesion (scrape/peel) results obtained are displayed in Table 4.

TABLE 4. ADHESION QUALITY OF COATING

Run No.	Titanium		Molybdenum		Copper	Adhesion
	Ion Plating Rate (b)	Bias Voltage (b)	Ion Plating Rate (b)	Bias Voltage (b)	Rate/Bias (a)	
1	H	H	H	H		Good
2	H	L	H	H		Good
3	H	L	L	H		Weak
4	H	L	L	L		Weak
5	H	H	H	L		Run aborted
6	H	L	H	L		Weak
7	H	H	L	L		Run aborted
8	H	H	L	H		" "
9	L	L	L	L		" "
10	L	H	L	H		Good
11	L	H	H	L		Weak
12	L	L	L	H		Run aborted
13	L	H	L	L		Weak
14	L	L	H	H		Run aborted
15	L	L	H	L		" "
16	L	H	H	H		Good

(a) 2500 Angstrom/minute at 300 watts RF bias

(b) H = high. L = low.

measurements. Very good adhesion (scrape/peel) qualities were obtained. A high temperature (1223 K) hydrogen treatment to diffusion bond coated BeO samples to copper tensile bars produced unsatisfactory results. The film failed upon removal of the tensile bars from the bonding fixture. The increase in substrate bias from 600 to 1000 watts improved coating/substrate adhesion (scrape/peel) qualities with no effect on high temperature bond performance.

Efficient rf power transfer to the beryllia substrate is critical if optimum coating adhesion and microstructure are to be obtained by ion plating. Power transfer is accomplished by a variable impedance transformer placed between the rf source and cathode. Under high vacuum conditions (10^{-5} Pascal), little if any power can be applied in an effective manner since there will not be sufficient ionization to form a plasma. The impedance of the cathode, which then looks like an antenna, will be high. With the design configuration used in this program it was possible to apparently transfer power to the cathode while at a pressure of 10^{-5} Pa. No plasma was observed. It was also possible to obtain a visible plasma in the 0.133-1.33 Pascal pressure range using argon. The values of the capacitances in the impedance transformer were very similar under these two conditions. These results indicate that the values of rf power truly used in the first two series of experiments may be other than that read on the gauge, i.e., the power was simply expended in heating the cooling water for the cathode.

If the cathode surface is reduced by interposing a properly designed ground shield, then ion bombardment of the beryllia will be improved, as should adhesion. A new ground shield arrangement with a 3.81 cm x 3.81 cm aperture was placed below the beryllia to increase the ion bombardment to its surface. The shield arrangement is illustrated in Figure 5.

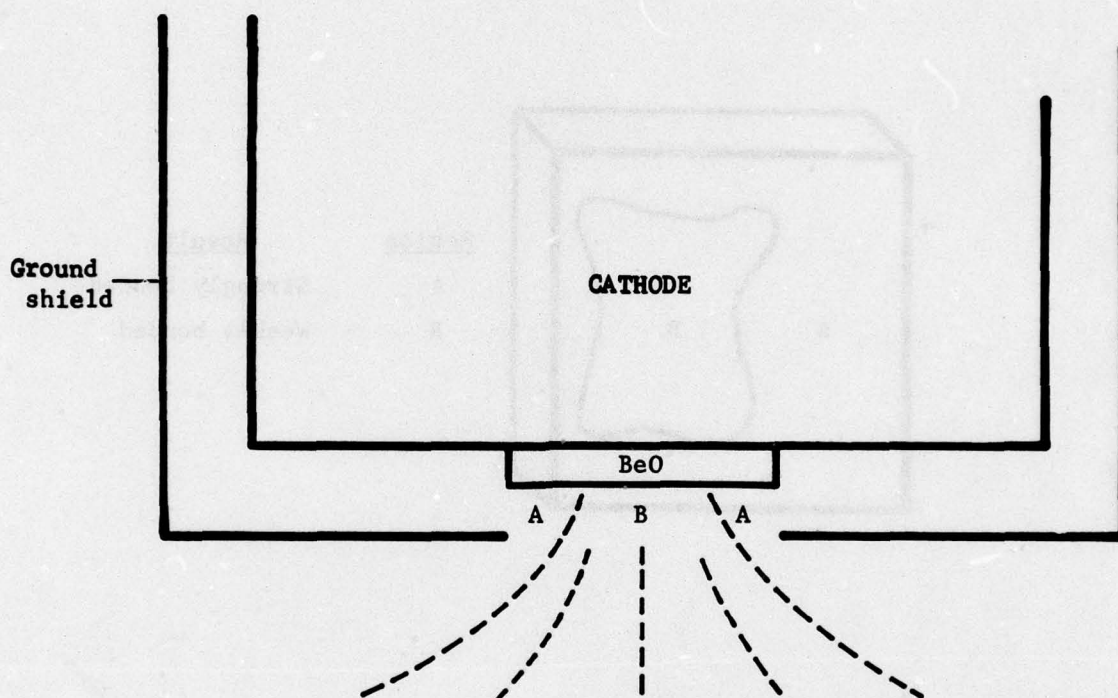


FIGURE 5. EFFECT OF DARK SPACE SHIELD ON ION PLATED COATING
 (Ion plated at an Argon pressure of 0.0666 Pascal)

With the shield in place, the Cu/Mo/Ti coating system was applied by ion plating to the 2.54 cm x 2.54 cm BeO wafer in the usual manner at 0.0666 Pascal. At this pressure the coating was affected as shown in Figure 6.

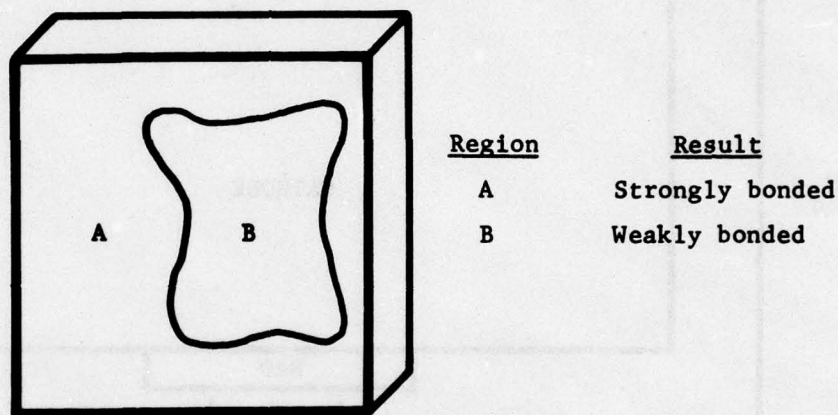


FIGURE 6. BONDING RESULTS FROM THE USE OF THE GROUND SHIELD

A scrape/peel evaluation of the applied coatings indicated a weakly adherent central region and an improved bond in the outer region.

It was concluded that, due to the shielding effect of the aperture and gas pressure, the outer region was not exposed to ion bombardment, and that the coating there was deposited under evaporation rather than ion plating conditions. X-ray fluorescence of the central area indicated molybdenum and copper in the peeled film, with titanium remaining on the BeO as shown in Figure 7.

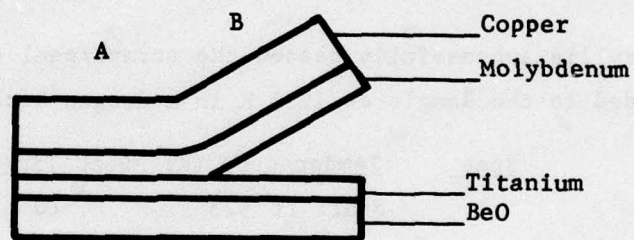


FIGURE 7. DIFFERENCE IN ADHESION BETWEEN REGION A AND REGION B

There was no obvious reason for this failure mode. Further experiments at gas pressures ranging from .665 Pa to 6.66×10^{-5} Pa substantiated that under evaporation conditions, good scrape/peel adherence could be obtained. In one of these experiments a sample was coated on both sides with evaporated titanium, molybdenum and copper under high vacuum conditions (10^{-5} Pa). The rates of evaporation and final film thicknesses are listed in Table 5.

TABLE 5
RESULTS OF EXPERIMENTS UTILIZING SIMPLE EVAPORATION

Material	Evaporation Rate, Angstrom/second	Film Thickness Angstroms
Titanium	26	1000
Molybdenum	26	7000
Copper	75	100,000

The coated beryllia successfully passed the scrape/peel test. Copper tensile bars were bonded to the sample at 1223 K in hydrogen according to the schedule:

<u>Step</u>	<u>Temperature (K)</u>	<u>Soak Time (min)</u>
1	Start at 573	10
2	Raise to 973	15
3	Raise to 1123	15
4	Raise to 1223	30
5	Cool to 723	60
6	Cool to 298	120

Following bonding, a test of tensile loading resulted in a maximum value of 35.08 Mega Pascal accompanied by unsatisfactory scrape/peel performance. The copper surface was also observed to be blackened. X-ray analysis of the elements on the copper surface indicated the presence of titanium, which meant a portion of the titanium adhesion layer had diffused into the copper and formed an intermetallic compound. A titanium layer thickness of 1000 A although providing excellent adherence to the BeO, is a sufficient reservoir to promote the diffusion through the molybdenum and copper.

A series of experiments were then performed to determine the effect of thickness of the titanium layer on diffusion through the molybdenum barrier layer and into the copper conductive film. The effects of dry or wet hydrogen were also studied as they relate to diffusion of titanium. Dry means hydrogen gas that has been passed through a commercial hydrogen drier and has a low dew point. For wet hydrogen experiments, a water bubbler was interposed between the braze fixture and dry hydrogen outlet.

A critical item for these experiments is the titanium thickness. Therefore, recalibration of the system for deposition rate, film thickness and gas pressure was performed using interferometry and optical transmission data to establish titanium thickness control. Both methods confirm the thickness reproducibility of films of titanium within an accuracy of ± 100 A. Optical transmission measurements for films 250 A thick had values of 15 percent \pm 5 percent, as measured by a densitometer. Having confirmed the calibration and repeatability of film deposition, several experiments involving thin and thick titanium adhesion layers were performed.

BeO substrates for these experiments were first air fired at 1273 K, then immediately placed in the vacuum system where they were sputter cleaned prior to coating. The two titanium thicknesses chosen were 250 A and 1000 A followed by 7000 A of molybdenum and 15,000 A of copper for all substrates. These substrates were 2.54 cm x 2.54 cm and, following coating, were cut into four samples for testing in dry and wet hydrogen. Any diffusion of titanium as a result of the processing would show up as a blackening in the copper layer. The results are given in Table 6.

TABLE 6
EFFECT OF HYDROGEN PROCESSING

	<u>Run No.</u>	<u>Titanium Thickness, A</u>	<u>Hydrogen Process, 1223 K</u>	<u>Results</u>
(1)	18, 19, 20	250	None	Bright copper
(2)	18, 19, 20	250	Wet - 2 hr.	Slight orange tint to copper
(3)	18, 19, 20	250	Dry - 2 hr.	Similar to results of (1)
(4)	32	1000	None	Bright copper similar to results of (1)
(5)	32	1000	Wet - 2 hr.	Slight change in copper coloration
(6)	32	1000	Dry - 2 hr.	Definite discoloration, darkening of copper film

The results indicate that (1) at thicknesses of 1000 Å of Ti, the overcoat of molybdenum (7000 Å thick) is not sufficient to reduce diffusion to an acceptable level and (2) decreased diffusion of titanium into copper was observed for wet hydrogen processing.

With the control necessary to accurately deposit desired thicknesses of titanium, two beryllia wafers were coated by high vacuum (10^{-5} Pa) evaporation techniques. The parameter values under which these samples were prepared and tensile loading data following high temperature hydrogen brazing are listed in Table 7.

TABLE 7
RESULTS OF HIGH TEMPERATURE BRAZING PROCESS

Experiment No.	Material	Thickness, Angstroms	1223 K Hydrogen Braze wet/dry	Tensile Loading Mega Pascal
46-47	Ti	250	Wet	147.3
	Mo	7000		
	Cu	100,000		
46-47	Ti	250	Dry	143.8
	Mo	7000		
	Cu	100,000		

These results were encouraging, but a scrape/peel test performed on a portion of each sample readily removed the coating. The adhesion had deteriorated following hydrogen braze processing to less than pre-braze conditions (157.9-166.6 Mega Pascal).

2. Titanium Diffusion

A barrier layer is needed between the titanium adhesion layer and copper conductive layer to prevent reaction of titanium and copper at high braze temperatures. This barrier layer can be a material which has low solubility for Ti or Cu, or can have a microstructure such that diffusion will be greatly impeded. Molybdenum has a low solubility for titanium up to 1155 K and for copper to 1223 K.

High temperature (1223 K) cycling, as experienced in the bonding operation of the Cu/Mo/Ti films (prepared as described in the above portion of this program), typically results in a degradation of film adherence. Various degrees of Cu-Ti interdiffusion were observed in the film layers after exposure to high temperatures, which suggested that the molybdenum was not functioning as a diffusion barrier. It was anticipated that the columnar microstructure of the Mo could be

responsible for its ineffective performance. Metallographic examination of the molybdenum layer revealed a columnar microstructure as suspected. In addition, cracks through the molybdenum film normal to the BeO surface were noted in the microstructure before high temperature treatment, which could provide short circuit paths for diffusion.

Since the molybdenum microstructure may have been responsible for the observed degradation of the film adherence after a high temperature treatment, an approach to improving the film performance would be to improve the metallurgical structure. A second possible approach would be to replace the titanium with another active metal that would not interdiffuse with copper.

A molybdenum-75 wt.% platinum alloy which should develop a two-phase microstructure was selected by the consultant, Professor R. Rapp, to increase the effectiveness of the barrier layer. Sputter depositing this alloy onto a substrate maintained at 303 K will produce a film which is fully dense and highly stressed. The recrystallization temperature for a film of this composition is normally in the range of 2073 to 2123 K⁹. However, this temperature will be significantly reduced as a result of the stresses developed during deposition under the noted conditions.¹⁰ A new recrystallization temperature in the range 873 to 1223 K was expected. However, this Mo-Pt layer was not heat treated prior to the deposition of the copper coating since this was not anticipated as being necessary with the subsequent high temperature brazing operation. As a result, when subjected to brazing at 1223 K in hydrogen, the Mo-Pt layer did not recrystallize properly, but rather allowed the previously observed diffusion and adhesion problems to occur. Thus, a valid testing of a two-phase barrier was not made.

Another approach recommended by the consultant was to replace the titanium with an iron-30 wt.% aluminum alloy. When vapor deposited from a liquid state (1850 K), the condensed film was initially expected to have a composition whose liquidus temperature would be ≈ 1200 K. This deposited Fe-Al alloy on beryllia would be followed by a coating of molybdenum and copper. Upon heat treatment to the brazing temperature, 1223 K, the Fe-Al would liquefy and, with aluminum being a major constituent, chemically bond to the beryllia.

A deposition rate for Fe-Al of 45 A/second was calculated based on the time necessary to deposit a 1000 A layer upon a circular substrate 6.45 cm² suspended 20.32 cm from the vapor source. A series of ten depositions were performed at different electron-beam power levels including that required to give a rate of 40 to 50 A per second which should have resulted in the desired composition. The deposits were collected on 2.54 cm x 2.54 cm glass slides and

analyzed by atomic absorption. The results listed in Table 8 indicate that the aluminum content of the vapor was higher than the predicted 30 wt/o Al.

TABLE 8
CHEMICAL ANALYSIS RESULTS FOR DEPOSITS
FROM AN Fe-30 wt.% Al SOURCE

	Iron		aluminum	
	w/o	at/o	w/o	at/o
(1)	51.86	34.24	48.13	65.76
(2)	55.83	37.92	44.16	62.08
(3)	50.23	32.77	49.76	67.23
(4)	56.91	38.95	43.08	61.05
(5)	68.38	51.09	31.61	48.91
(6)	69.76	52.72	30.23	47.28
(7)	48.37	31.16	51.62	68.84
(8)	43.49	27.08	56.60	77.92
(9)	47.97	30.82	52.02	69.18
(10)	49.62	37.25	40.37	62.75

A temperature profile of the Fe-Al evaporation source was determined for both input electron-beam power and evaporation rate. Temperatures of the evaporant up to 1620 K and rates to 75 A per second were measured.

One experiment was performed to deposit the Fe-Al to replace titanium as an active adhesion coating to BeO. However, subsequent testing indicated weak adhesion. It is presumed that the Fe-Al coating composition was in the range of those tabulated above, which may account for the weak bond. The mechanism for adhesion of Fe-Al to BeO relies on a wetting action of the alloy at the braze temperature. As the alloy melts, a reaction is expected to occur. However, the composition of 50-50 w/o Fe-Al has a melting point above the normal braze temperature, and thus melting and subsequent bonding would not have taken place. The expected result for Fe-Al was not verified since the composition of the condensate necessary to melt at ≈ 1200 K could not be attained. This was apparently due to the formation of FeAl_2 in the vapor, at the substrate, or in the molten pool.⁵

Both approaches described above were unsuccessful. Although a Mo-Pt alloy could be deposited, no microstructural change was achieved. The expected result for Fe-Al was not verified since the composition of the deposited film could not be controlled in any manner other than as described herein.

Thus far all of the coatings applied by evaporation techniques were condensed onto substrates maintained at low temperatures, <573 K, which according to the Movchan and Demchishin¹ (M & D) diagram, Figure 8, are Zone 1 coatings characterized by a porous structure consisting of tapered crystal-lites separated by voids. Although it is true that adherent coatings were deposited, the microstructure, particularly that of the molybdenum was not adequate to prevent diffusion reactions from occurring between titanium and copper at 1223-1273 K.

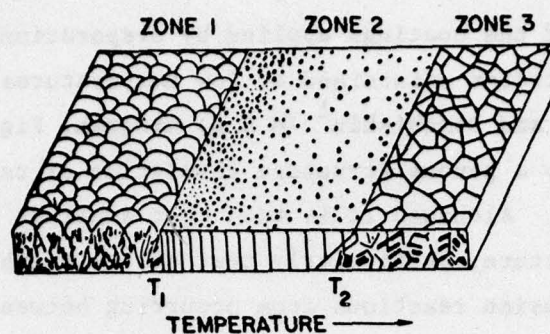
For copper, molybdenum, and titanium, a change in condensate structure from open (Zone 1) to dense columnar (Zone 2) requires the substrate temperatures shown in Table 9. The design of the cathode allowed only a 300 watt heater to be installed with the capability of heating the substrate to a maximum of 800 K. A substantial change in cathode design would have been required to optimize the structure of the evaporated coatings through increased temperature. Coatings applied by ion plating can potentially suppress the Zone 1 structure at low substrate temperature as suggested by Bland, Kominiak, and Mattox⁶. The film structure/temperature problem thus seemed best solved by a return to the ion plating process.

TABLE 9
ZONE TRANSITION TEMPERATURES

Material	T_{mp} (K)	Transition Temperatures (K)	
		Zone 1-2	Zone 2-3
Ti	1668	582 ($0.3 T_{mp}$)	71 ($0.5 T_{mp}$)
Mo	2883	865	1442
Cu	1356	407	678

$T_{mp} = T_m$ = melting temperature

As determined earlier, the efficient transfer of rf power to the beryllia substrate during ion plating was not optimized. The rf power transferred to the substrate is dependent on the ability to continuously match the output impedance of the generator to that of the plasma. The total pressure of the gas influences the degree of ionization and thus higher gas pressures



	ZONE 1	ZONE 2	ZONE 3
METALS	$<0.3 T'_m$	$0.3 - 0.45 T'_m$	$>0.45 T'_m$
OXIDES	$<0.26 T'_m$	$0.26 - 0.45 T'_m$	$>0.45 T'_m$

Transition Temperatures Between Various Structural Zones

Material	Melting Temp. $T_m(^{\circ}\text{K})$	$T_1(^{\circ}\text{K})$	$\frac{T_1(^{\circ}\text{K})}{T_m(^{\circ}\text{K})}$	$T_2(^{\circ}\text{K})$	$\frac{T_2(^{\circ}\text{K})}{T_m(^{\circ}\text{K})}$	Reference
Ti	1945	653 ± 10	0.3	923	0.5	Movchan and Demchishin ⁽⁴⁾
Ti	1945	673 ± 20	0.31	phase transformation overlaps		Bunshah and Juntz ⁽⁴²⁾
Ni	1726	543 ± 10	0.3	723 ± 10	0.45-0.5	Movchan and Demchishin ⁽⁴⁾
Ni	1726			777 ± 20	0.45	Kane and Bunshah ⁽⁴³⁾
W	3683	1133 ± 50	0.3	1723 ± 50	0.45-0.5	Movchan and Demchishin ⁽⁴⁾
Mo	2883	923 ± 20	0.3-0.34	1200	0.44	Sherman and Bunshah ⁽³⁷⁾
Fe	1810			phase transformation overlaps		Kennedy ⁽⁴⁶⁾
Be	1573	473 ± 20	0.29	1023 ± 50	0.63	Mah and Nordin ⁽⁴⁵⁾
Ni-20Cr	1673	500 ± 50	0.3	870	0.52	Agarwal, Kane and Bunshah ⁽⁴⁴⁾
ZrO ₂	2973	648 ± 10	0.22	1273	0.45-0.5	Movchan and Demchishin ⁽⁴⁾
Al ₂ O ₃	2323	623 ± 10	0.26	1173	0.5	Movchan and Demchishin ⁽⁴⁾
TiC	3340	1070 ± 30	0.31	Not observed up to 1723 ^o K or 0.51 T_m		Raghuram and Bunshah ⁽³⁰⁾
NbC	Obeys the Movchan-Demchishin Model					Paton, Movchan and Demchishin ⁽²⁸⁾
ZrO ₂	Obeys the Movchan-Demchishin Model					Paton, Movchan and Demchishin ⁽²⁸⁾

NOTE: From structures observed at a specific deposition temperature, Au-Cu⁽⁵⁸⁾ and V⁽³⁷⁾ appear to obey the Movchan-Demchishin Model.

FIGURE 8. MOVCHAN-DEMCHISHIN STRUCTURE-TEMPERATURE DIAGRAM⁸

ionization for the present cathode design and thus higher gas pressures result in more ionization which lowers the plasma impedance. A critical experiment involving gas pressure as a variable was performed to determine whether the plasma impedance could be lowered sufficiently to effect a more efficient transfer of rf power. The efficiency was measured in terms of the ability to heat the substrate by ion bombardment. The results, given in Table 10, confirmed the previous conclusions, i.e., that the rf power transferred to the substrate was unusually low in the ion plating experiments to this point, due to the inadequate cathode design.

TABLE 10
SUBSTRATE TEMPERATURE AS A FUNCTION OF RF POWER
AND GAS PRESSURE

Argon Pressure, Pascal	RF Power, watts/cm ²	Time, min.	Temperature, K
1.064	248	60	<773
3.99	93	10	1173-1273

A modification to the M & D diagram by Thornton⁷ suggests that as the gas pressure increases the temperature requirement for each zone also increases. As an example of this, a material deposited onto a substrate maintained at a temperature of 0.4 T_m will have a Zone 2 structure consisting of columnar grains when deposited at a pressure <3.3 Pa. As the gas pressure is increased to 4 Pa, a Zone 1 structure, characterized by tapered crystallites separated by voids, results for the same substrate temperature, 0.5 T_m.

Due to the initial problems with inadequate rf power transfer, a Zone 2 structure could not be obtained. The gas pressure/structure considerations mentioned above augmented the difficulty.

Accordingly, an effort was outlined to identify the factors that contributed to the work adherence obtained thus far. In addition to evaluating the effect of various coating conditions on the adherence of the Cu/Mo/Ti system to the BeO, it was decided to examine the bond strength of each individual

layer to better understand the problems being encountered. A summary of the coating conditions studied in selected experiments, with a brief explanation of the objective is given in Table 11. Conditions were chosen to isolate the problem of weak bond strength in the metal-to-ceramic system chosen.

In Table 12, a summary is listed which includes the scrape/peel test data, and tensile test data resulting from epoxy and high temperature bond strength evaluations. These can be grouped so that experiments 100 through 110 indicate that improved adhesion between copper and molybdenum has been obtained using purified argon, and that oxygen sputter cleaning of the BeO prior to ion plating did not improve results.

In Experiment 111, even though optimum conditions were used, scrape/peel results were similar to earlier work. The molybdenum barrier layer was still ineffective and the substrate temperature was still not adequate to alter the columnar structure.

At this point, it was decided to eliminate titanium and to deposit molybdenum directly onto BeO to eliminate interdiffusion effects. Experiments 114 through 121 indicate that molybdenum can be deposited onto BeO with good adherence but when Cu is ion plated on molybdenum-coated BeO, poor adherence results at the copper/molybdenum interface. After observing the brittle molybdenum material removed in a scrape/peel test from Experiment 114, a polishing procedure was initiated in an attempt to remove this brittle surface layer prior to deposition of copper. Metallographic polishing with submicron diamond powder produced a mirror-like surface.

Experiments 121 confirms the good adhesion results obtained following polishing. High temperature vacuum brazing resulted in a tensile strength value of 147.3 Mega Pascal without the use of active metal adhesion aid such as titanium. This is a particularly important result.

3. Coating Structure Analysis

An AMR 1000 Scanning Electron Microscope which has a resolution of 200 Å and is equipped with a Princeton Gamma Tech dispersive X-ray detector was used to quantify the chemical composition of an ion-plated Ti, Mo, and Cu coating combination on BeO from Experimental Run 114. The sample selected was deposited under conditions expected to yield optimum adhesion, i.e., sputter etching,

TABLE 11
SUMMARY OF COATING CONDITIONS EVALUATED FOR
SELECTED EXPERIMENTS

Run No.	Coating Conditions Evaluated	Objective
100	(1) commercial high-purity argon (2) low-substrate temperature	Establish standard coating adhesion data
102	(1) commercial high-purity argon (2) low-substrate temperature	ditto
103	(1) commercial high-purity argon (2) low-substrate temperature	"
109	(1) hot-titanium getter purified argon (2) low-substrate temperature	Elimination of oxygen and nitrogen effect on titanium
110	(1) hot-titanium getter purified argon (2) oxygen as sputter cleaning gas (3) low-substrate temperature	Elimination of oxygen and nitrogen effect on titanium in addition to removal of residual hydrocarbon contamination on the BeO surface
111	(1) hot-titanium getter purified argon (2) high substrate temperature	Improve adhesion of metal layers
114	(1) hot-titanium getter purified argon (2) high-substrate temperature	Maximize adhesion of Mo without Ti
118	(1) polished molybdenum on BeO (2) high substrate temperature (3) hot-titanium getter purified argon (4) copper deposited by ion plating	Maximize adhesion of Cu on Mo/BeO
119	(1) hot-titanium getter purified argon (2) high substrate temperature (3) polish of molybdenum following coating	Preparation of pull test sample

TABLE 12
SUMMARY OF DATA FOR SELECTED EXPERIMENTS UNDER VARIOUS COATING CONDITIONS

Run No.	Substrate	Coating Material	Coating Condition Evaluated	Scrape Adhesion Tests	Bond Type	Tensile Strength, Mega Pascal
100	BeO	Ti	Low substrate temperature <473 K No Ar purifier	Good	Epoxy	>157.9
102	BeO	Ti, Mo	Low substrate temperature <473 K No Ar purifier	Good	Epoxy	>157.9
103	BeO	Ti, Mo, Cu	Low substrate temperature <473 K No Ar purifier	Poor Cu adhesion	--	--
109	BeO	Ti, Mo, Cu	Low substrate temperature <473 K Purified argon	Good	Epoxy	>157.9
110	BeO	Ti, Mo, Cu	Low substrate temperature <473 K O ₂ sputter cleaning Purified argon	Some peel	Epoxy	>157.9
111	BeO	Ti, Mo, Cu	High substrate temperature 1173 - 1273 K - Purified argon	Some peel	--	--
114	BeO	Mo	High substrate temperature 1173 - 1273 K - Purified argon	Good; some brittle Mo on surface removed	--	--
118	BeO, Mo (114)	Cu	Mo polished and coated with copper; purified argon (high temperature)	Good	--	--
119	BeO	Mo	High substrate temperature 1173 - 1273 K; Purified argon, Mo coating polished to mirror-like finish	Good	--	--
121	BeO, Mo (119)	Cu	High substrate temperature 1173 - 1273 K; Purified argon	Good	Copper-copper H ₂ (1223 K) Vacuum bonded (1223 K)	68.4 147.3

vacuum outgassing of the BeO at 1173-1273 K, ion plating of Ti, Mo, and Cu onto the BeO substrate held at 1173-1273 K, 10^{-5} Pa in the coating chamber prior to ion plating, purification of the argon gas through a copper and titanium getter operating at 973 K, and an initial air bake of the BeO at 1273 K. As a precautionary measure to eliminate any recontamination of the BeO or coatings deposited, the bias voltage used for sputtering was maintained uninterrupted throughout the deposition cycle. The coated BeO was sectioned metallographically to show the microstructure of the Ti, Mo, and Cu deposits. Noteworthy in the structure shown in Figure 9 are two features (1) the equiaxed copper grain growth, which is the as-deposited structure, and (2) an area of porosity near the copper-molybdenum interface.

An SEM X-ray image of the BeO, Ti, Mo, Cu specimen, in cross section, was taken (Figures 10 and 11). The pores in the copper coating nearest to the molybdenum are clearly shown, as is the columnar structure of the molybdenum. An elemental analysis (Figure 12) of the coatings (Figure 13) in the area of a pore and adjacent area indicates a slightly higher concentration of titanium in the pore wall than in the adjacent area. To obtain this information a stationary high resolution 70 A electron beam was focused in the suspect pore. Spot counting of the X-rays emitted produced a continuous energy spectrum of the elements present. The stored spectrum is represented by the vertical bars in Figure 12. A similar spectrum was taken for an adjacent area. Horizontal bars indicate the spectrum from this area. The titanium enrichment of the pore walls is not understood.

The molybdenum barrier layer was analyzed in a similar way (Figure 14). In addition to molybdenum being detected, traces of both titanium and copper were present. The columnar structure of the molybdenum layer on BeO is shown in Figure 15. This was a high temperature (1173-1273 K) ion plated coating (Experimental Run No. 114) directly onto BeO. A comparison of the molybdenum and copper structures (Figure 15, Figure 9) with the Movchan and Demchishin temperature/structure-dependence diagram (Figure 8) verifies the need for minimum substrate temperatures of 1173-1273 K for the transition to equiaxed grain growth of molybdenum.²

The molybdenum under present deposition conditions is ineffective as a barrier layer. In Figure 11, a high magnification (20,000X) SEM micrograph reveals the columnar growth of the molybdenum as deposited with copper at 1173-1273 K. The interface region between the molybdenum and copper is

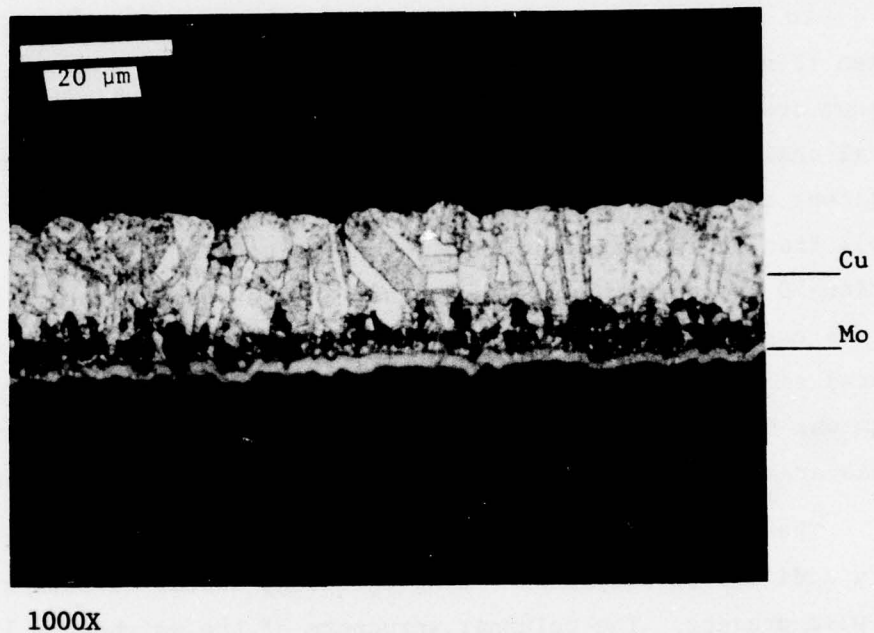
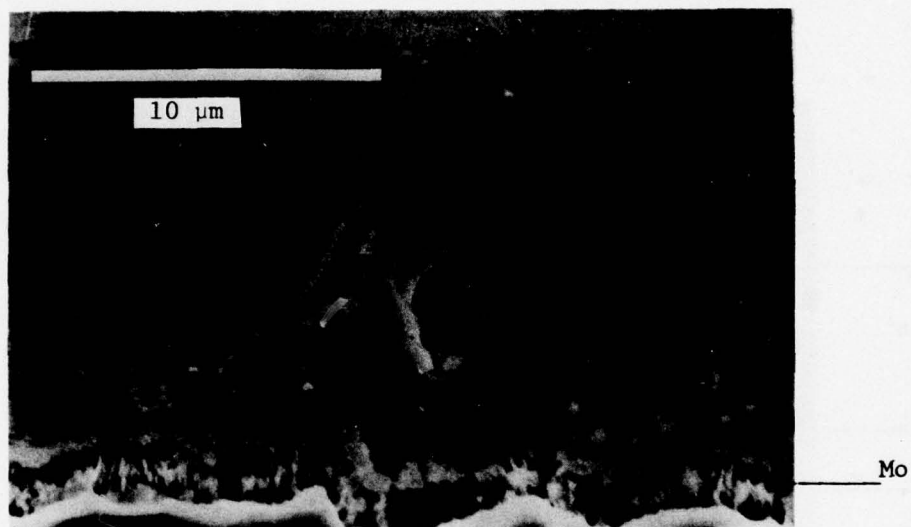


FIGURE 9. RUN 111 MICROSTRUCTURE OF COPPER MOLYBDENUM AND TITANIUM ON BERYLLIUM OXIDE, ION PLATED AT A TEMPERATURE OF 1173-1273° K



5010X

FIGURE 10. RUN 111 SCANNING ELECTRON MICROGRAPH OF ION PLATED COPPER, MOLYBDENUM, TITANIUM ON BERYLLIUM OXIDE, SHOWING VOIDS IN COPPER DEPOSIT AND COLUMNAR STRUCTURE IN THE MOLYBDENUM

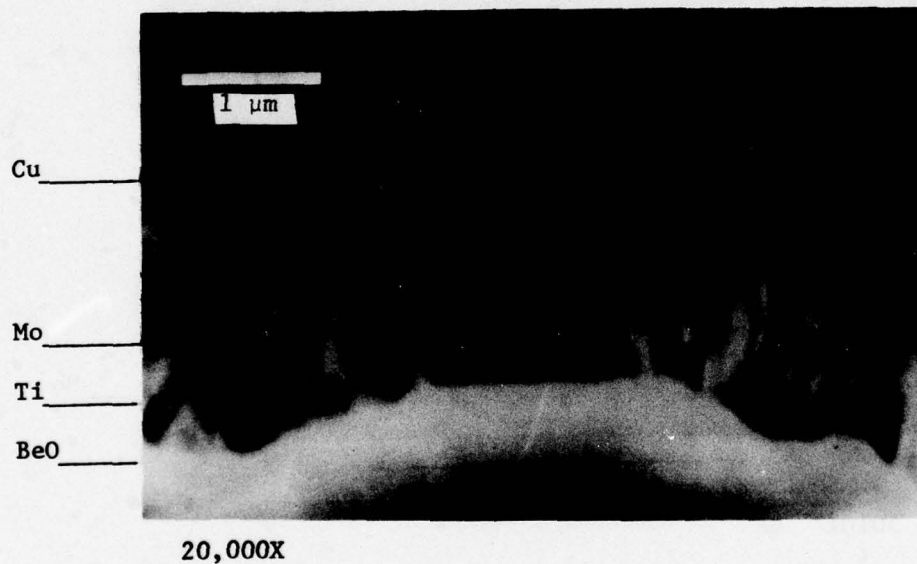


FIGURE 11. RUN 111 SCANNING ELECTRON MICROGRAPH SHOWS COLUMNAR STRUCTURE OF THE MOLYBDENUM BARRIER LAYER

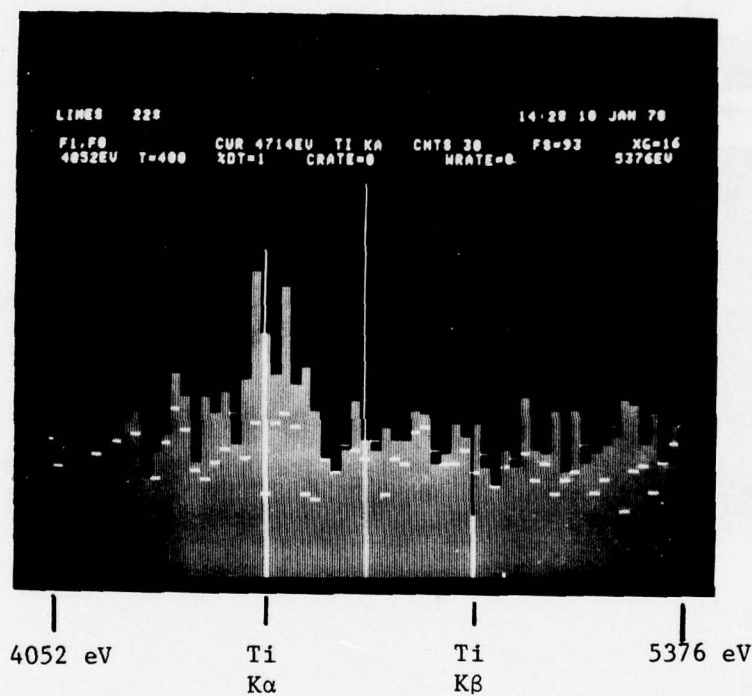


FIGURE 12. RUN 111 TITANIUM CONCENTRATION IN PORE WALL (VERTICAL BARS) VS ADJACENT AREA (HORIZONTAL BARS)



2000X

FIGURE 13. RUN 111 SCANNING ELECTRON MICROGRAPH OF COPPER, MOLYBDENUM, AND TITANIUM ON BERYLLIUM OXIDE SHOWING VOID STRUCTURE

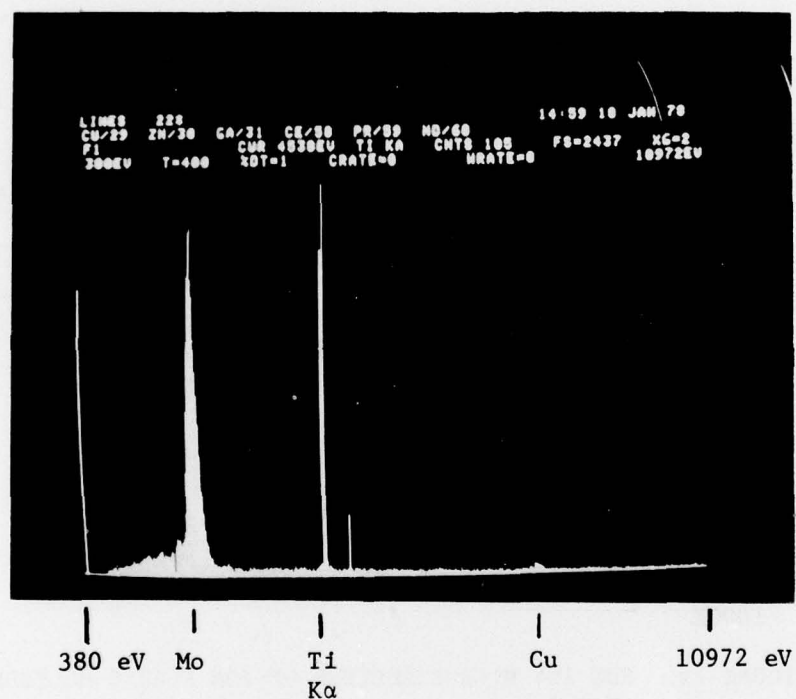


FIGURE 14. RUN 111 CHEMICAL ANALYSIS BY ENERGY DISPERSIVE X-RAY TECHNIQUE TO IDENTIFY COMPOSITION OF MOLYBDENUM BARRIER LAYER (The two vertical marker bars in the titanium area are not to be confused with the peak bright)

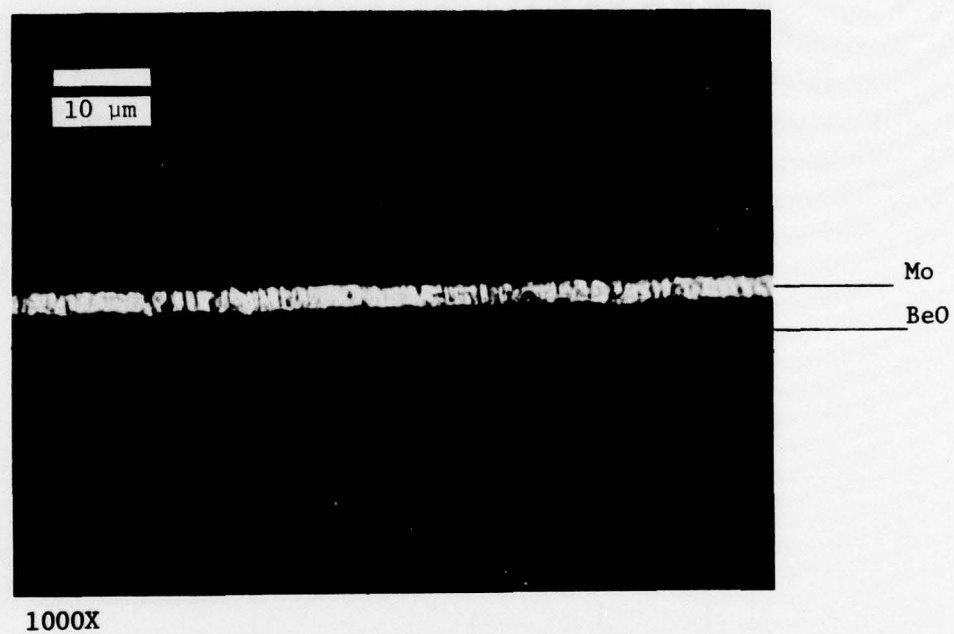


FIGURE 15. RUN 114 MICROSTRUCTURE OF ION PLATED MOLYBDENUM
ON BeO

composed of a whisker-like molybdenum structure covered by a blanket of copper. A scrape test performed on this sample resulted in removal of copper, leaving what appeared to be molybdenum. The brittle nature of the whisker-like molybdenum-copper interface is masked to some extent by the ductility of the copper. A molybdenum-on-BeO coating (Run 114), similarly tested, exhibited the same qualitative brittle nature. The amount of brittle molybdenum observed as a result of continuous scrape tests in the same area of the specimen did decrease. A metallographic polishing procedure was then used on the molybdenum coating prepared in Run 119. The Linde A & B polishing material used in conjunction with a vibratory polisher produced a specular molybdenum surface as opposed to the diffuse as-coated appearance. Another scrape test indicated that most of the whisker-like structure was removed by polishing. Following an ultrasonic solvent cleaning to remove any polishing compound, a copper layer was deposited by ion plating. Two tensile specimens were then prepared from Run 121 and bonded, one in hydrogen at 1223 K, the other in vacuum, also at 1223 K. Uniaxial tension testing was performed with the following results.

<u>Bond Failure Location</u>	<u>Bond Tensile Strength, Mega Pascal</u>	<u>Bond Atmosphere</u>
Ceramic/film interface	68.51	Hydrogen (1223 K)
Entirely in ceramic	146.56	Vacuum (1223 K)

The reason for degradation of bond strength as a result of the high temperature hydrogen cycle is unknown at present.

4. Aluminum Nitride

For this study, a 99.7 percent purity AlN powder was procured from Cerac, Inc. The vendor-supplied analysis indicated that major impurities were O₂ (0.3 percent), C (0.035 percent), and Si (0.030 percent). Particle-size distribution analysis showed that the powder was essentially -200 mesh (<74 μ meter). Oxygen analysis by inert gas fusion showed the powder to contain 5 percent O₂ which is considerably higher than quoted. Some of the powder was passed through an air classifier to remove the coarser particles. The particle size distribution of the classified powder showed that 90 percent of the classified powder was <10 μ meter. The oxygen content of this powder was found to be 6 percent, probably due to the higher surface area of this fraction of the powder.

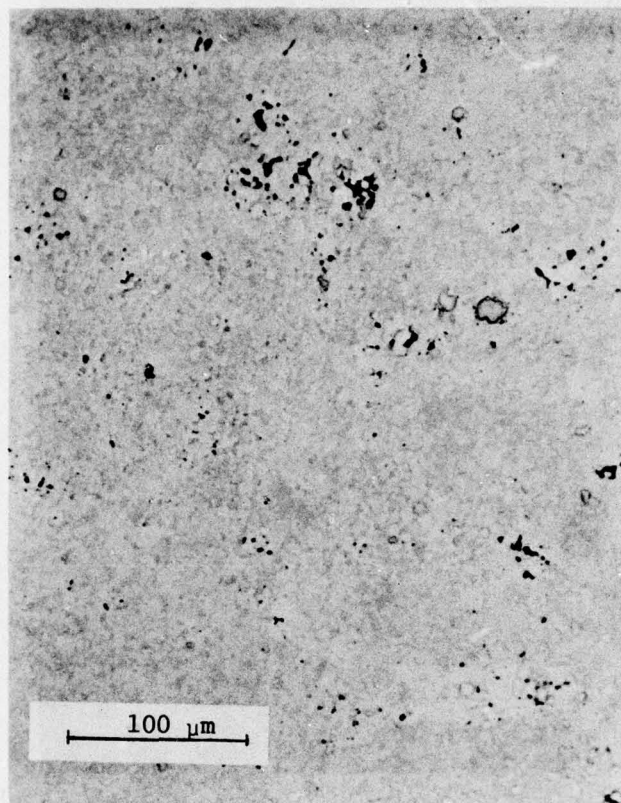
Three initial hot pressings were performed as detailed in Table 13. Densification generally commenced at ~ 1700 K and was complete after 5 minutes at the final temperature, indicating that transient liquid phase sintering was the densification mechanism.

TABLE 13
EXPERIMENTAL HOT PRESSING CONDITIONS WITH AS-RECEIVED
AND -10μ AlN POWDERS

Powder	Temperature, K	Pressure, Mega Pascal	Time at Temperature, min.	Density, g/cm^3
1. As received	2200	140.0	5	3.238
2. Classified	2144	140.0	5	3.361
3. Classified	2227	175.4	30	3.266

Figure 16 shows the microstructure of the sample fabricated using the as-received powder. Low porosity is readily apparent. In contrast, Sample No. 3 fabricated from the -10μ powder, has a more uniform microstructure (see Figure 17). The apparent two-phase nature of the sample is considered to be primarily due to textural effects. One or two inclusions (the white spots in Figure 17) however, still remain in the sample. X-ray diffraction analysis indicated the presence of a small amount of a second phase, which was thought to be Al_2O_3 in view of the powders 6 percent oxygen content.

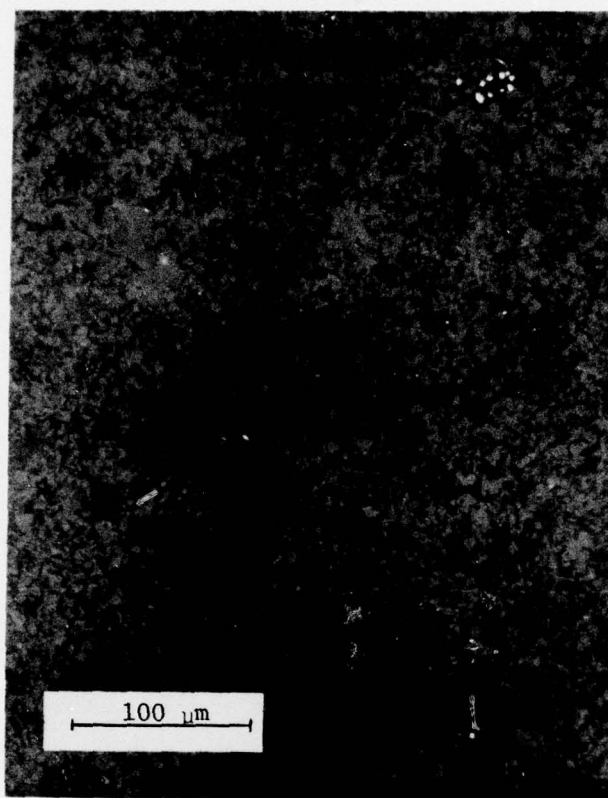
The thermal conductivity values for samples from the first and third hot pressings were 0.185 and 0.195 watts/cm $^\circ\text{K}$, respectively using the comparator method. In order to determine the thermal conductivity values more precisely, a small disc from Sample No. 3 was prepared, and its thermal diffusivity determined at selected temperatures from room temperature to 981 K. The thermal conductivity values, presented in Table 14, are considerably below the minimum acceptable value for a candidate substrate material.



X250

8H725

FIGURE 16. GENERAL MICROSTRUCTURE OF AlN HOT PRESSED
USING VENDOR'S POWDER



X250

8H892

FIGURE 17. GENERAL MICROSTRUCTURE OF AlN HOT PRESSED
USING THE -10 μm FRACTION OF VENDOR'S
POWDER

TABLE 14
THERMAL CONDUCTIVITY AND DIFFUSIVITY OF AlN

Temp. (° K)	K (Watts/cm ^{-° K})	α (cm ² /sec)
290	0.176	0.077
568	0.173	0.050
795	0.149	0.040
981	0.135	0.035

In order to fabricate an acceptable AlN substrate material two problems needed to be addressed. The preparation of low oxygen content AlN and the preparation of a dense (preferably 100%) material. Three approaches were initial considered: (1) Active oxidation of Al₂O₃ from the AlN powder, (2) carbon reduction by the reaction $\text{Al}_2\text{O}_3 + 3\text{C} + \text{N}_2 \rightarrow 2\text{AlN} + 3\text{CO}$, and (3) formation of an AlN solid solution.

The first approach was ruled out on thermodynamic grounds based on data from JANAF tables. Mg₃N, Li₃N, Li₂SiN₃, and Be₃N₂ were suggested as possible additives for incorporating oxygen into AlN as a solid solution, and, after discussions with AFML, Be₃N₂ was selected for further study. Attempts to improve the thermal conductivity of AlN were thus directed to using carbon and Be₃N₂ to remove the second phase Al₂O₃.

Based on thermodynamic calculations for the reaction $\text{Al}_2\text{O}_3 + 3\text{C} + \text{N}_2 \rightarrow 2\text{AlN} + 3\text{CO}$, the data listed in Table 15 show that this reaction can go to virtual completion at 2103 K. Carbon black (1.8 g), which had been previously heated at 453 K to remove adsorbed H₂O, was mixed with 20 g AlN in n-hexane, then dried and hot pressed in N₂ at 2128 K for 30 mins. It appeared that the carbon black mixed easily with the AlN and the resulting hot pressed disc had an expected dark appearance. However, in contrast to the previous pressing, the sample was not fully dense (3.11 g/cm³, 95.47 percent theoretical density), possibly as a result of some reaction and removal of the liquid phase necessary to promote densification. Figure 18 shows that this material contained agglomerated unreacted carbon black particles. Reaction between the carbon black and the oxide does not appear to have occurred. The lower

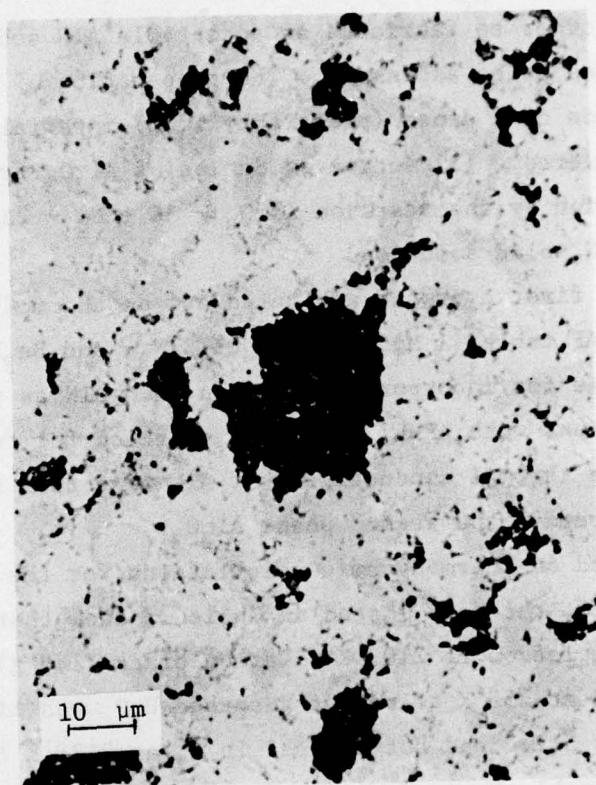


FIGURE 18. MICROSTRUCTURE OF HOT PRESSED AlN POWDER WITH ADDITION OF C POWDER.

Based upon the presence of agglomerated, unreacted particles, the reaction did not occur.

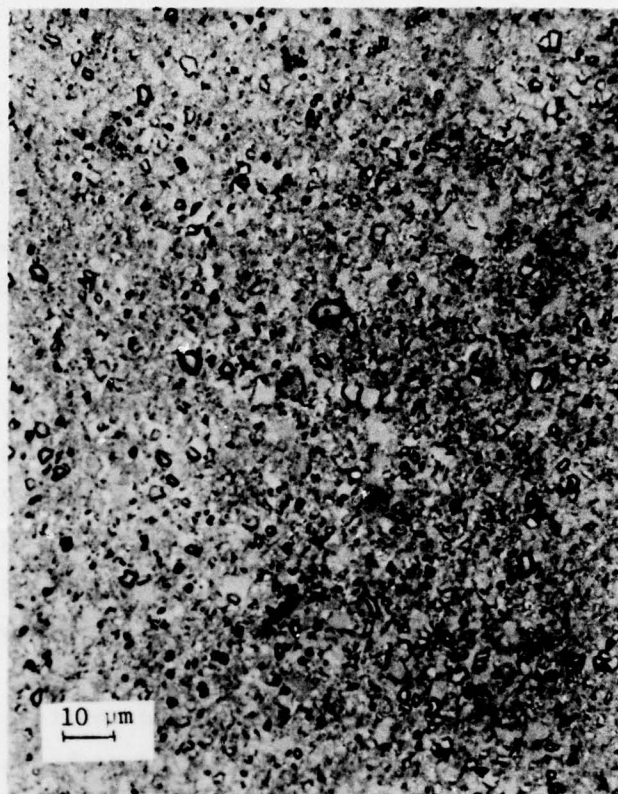
density of this sample is consequently considered to be due to the presence of the lower density carbon (density 2.3 g/cm^3) rather than to partial densification.

TABLE 15
EQUILIBRIUM COMPOSITION (MOLES) FROM 1 MOLE Al_2O_3 AND
3 MOLES C AND 1 MOLE N_2 AT TEMPERATURES INDICATED

Elements and Compounds	Mole Fractions at 1 atm. Total Gas Pressure						
	Temperature, K						
	1227	1327	1427	1527	1627	1727	1827
AlN (s)	0.00192	0.00608	0.01695	0.04328	0.10366	0.22049	0.34028
Al ₂ O ₃ (s)	0.19904	0.19696	0.19153	0.17836	0.14817	0.08974	0.02950
C (s)	0.59711	0.59088	0.57458	0.53508	0.44451	0.26922	0.08866
CO (g)	0.00289	0.00912	0.02542	0.06491	0.15549	0.33076	0.51123
N ₂ (g)	0.19904	0.19696	0.19153	0.17836	0.14817	0.08975	0.02983

In order to facilitate better mixing and to utilize a more active carbon source furfuryl alcohol was used instead of carbon black. Phthalic anhydride was used as a catalyst in the polymerization of the furfuryl alcohol. The mixture was prepared in acetone, dried, die pressed and heated at 115°C for 12 hrs, before hot pressing at 1970°C for 1 hour at 175.4 Mega Pascal. Final sample density was 3.17 g/cm^3 . A dark phase (see Figure 19) appears to coat many of the large AlN grains suggesting that reaction may not have occurred.

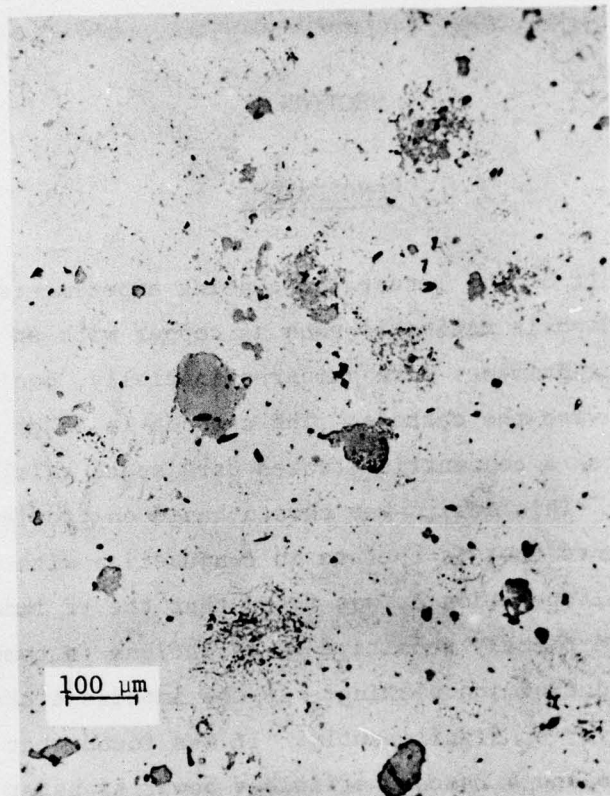
One experiment with Be_3N_2 (oxygen content 6.2 percent) was performed. A mixture of 20 gms AlN and 2 gms Be_3N_2 was hot pressed at 2223 K and 175.4 Mega Pascal to give a dense product (density 3.24 g/cm^3). The two phase nature of this material is shown in Figure 20. If the Be_3N_2 had reacted, it should form a solid solution in the AlN and consequently form a homogeneous solid. This has clearly not occurred.



X750

OJ786

FIGURE 19. AlN HOT PRESSED WITH FURFURYL ALCOHOL
AS THE CARBON SOURCE



X250

OJ792

FIGURE 20. GENERAL MICROSTRUCTURE OF AlN HOT PRESSED
WITH TEN PERCENT Be_3N_2

The lack of reaction of the carbon and Be_3N_2 additives with the Al_2O_3 present in the AlN was also confirmed by the thermal conductivity measurements. No improvement over the value for the sample hot pressed from the -10μ AlN powder was found.

SECTION V

CONCLUSIONS

As a result of the latest ion plating experiments, techniques have been developed to deposit materials such as copper with an equiaxed structure. These ion plating experiments were hampered initially, due to a design problem associated with the cathode. The cathode is 35 cm long x 13 cm in diameter and requires a concentric Crookes dark space shield of nearly similar dimensions. This design was chosen based on previous work and the added requirements that it operate in conjunction with a chamber attached loadlock. In actual operation it was found that the rf impedance presented by this design was extremely sensitive to variations in temperature and/or the argon pressure during ion plating. As the impedance changes, the rf powder transferred varies significantly. It was found that for an argon pressure between 2.6 and 4 Pascal, efficient power transfer could be attained. However, plasma instabilities still occurred, and this made it necessary to continually adjust the variable impedance transformer (matching network) to maintain some semblance of a high deposition energy process.

Molybdenum and copper were successfully ion plated onto BeO , with and without an interlayer of titanium, resulting in a metal-to-ceramic bond of high strength. However, the structure and whisker-like surface character of the molybdenum as deposited at 1173-1273 K was not adequate for strong copper adhesion. Removal of the whisker-like surface of the molybdenum by polishing was found to be necessary for good copper adhesion. Either an increase in substrate temperature should eliminate this problem and produce equiaxed grain growth or a proper redesign of the cathode.

Dense, uniform AlN was obtained by hot pressing $-10\text{ }\mu\text{m}$ AlN powder at 2223 K and 175.4 Mega Pascal for 30 mins. Due to the oxygen present in the starting powder, the thermal conductivity of the compacted material is substantially below that desired for a candidate substrate material. Attempts to overcome this problem by removal of oxygen on incorporation into an AlN solid solution using Be_3N_2 were not effective because significant reaction did not occur.

SECTION VI

RECOMMENDATIONS

Effective metal-to-ceramic bonds between BeO and molybdenum can be produced without titanium as an adhesion aid. The preferred conditions are:

- (1) High substrate temperature, minimum 1173-1273 K, for molybdenum and copper deposition by ion plating
- (2) Sputter-cleaning and high-temperature (1173-1273 K) vacuum degassing of BeO.

It is recommended that an automatic variable impedance transformer (matching network) be used with the rf ion plating system. This would constantly optimize the rf power transfer to the substrate. Such a device is being purchased. Further, it is recommended that a properly designed cathode should be fabricated.

The extreme difficulty experienced in attempts to remove oxygen from commercial AlN powder indicates that an ultra-fine, high-purity, low-oxygen content starting powder is required. Methods of preparing such a powder should be evaluated. As the presence of oxygen aids the densification process, a low oxygen content powder may be difficult to consolidate without additives. It is recommended that additive concentrations be quite low (0.5 percent) so that the thermal conductivity is only marginally affected.

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